

I hereby certify that this New Application Transmittal and the documents referred to as enclosed therein are being deposited with the U. S. Postal Service on **MAY 22, 2001**, in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number EF088565305US , addressed to: Assistant Commissioner for Patents, Box Patent Application, Washington, D.C. 20231.

TPEvang  
Person Making Deposit

"Express Mail" Mailing Label No. EF088565305US

By

655 Stoney Creek,  
Livermore, CA 94550

698 Old Oak Road,  
Livermore, CA 94550

CITIZENS OF THE UNITED STATES OF AMERICA

# ORGANIC MATERIALS AND DEVICES FOR DETECTING IONIZING RADIATION

## STATEMENT OF GOVERNMENT INTEREST

This invention was made with Government support under contract no. DE-AC04-94AL85000 awarded by the U. S. Department of Energy to Sandia Corporation. The Government has certain rights in the invention.

## BACKGROUND OF THE INVENTION

The present invention is directed generally to a class of organic semiconductor materials useful for the direct detection of ionizing radiation namely,  $\pi$ -conjugated molecules, and particularly  $\pi$ -conjugated polymers and polyaromatic hydrocarbons. The invention further relates to apparatus for detecting and measuring ionizing radiation.

Generally, semiconductor detectors of nuclear radiation operate by exploiting the fact that incident radiation, by interaction in the detector material, will create a charge pulse consisting of holes and electrons that can be separated under the influence of an electric field and the current detected by an external circuit.

Because they are readily available, radiation detector materials are generally semiconductor materials such as Si or Ge with lithium introduced into the semiconductor material so that it behaves as an extrinsic semiconductor. However, these materials have less than ideal band gap widths and high dark currents making them unattractive candidates for room temperature radiation detection devices. Further, the need to keep such Si(Li) and Ge detectors cooled to cryogenic temperatures poses significant limitations on the use of these materials in many applications, particularly where portability is desired.

Certain nonmetallic, crystalline solids such as mercuric iodide ( $\text{HgI}_2$ ), lead iodide ( $\text{PbI}_2$ ), thallium bromide ( $\text{TlBr}$ ), indium iodide ( $\text{InI}$ ), thallium bromoiodide ( $\text{TlBrI}$ ),

mercuric bromoiodide ( $\text{HgBrI}$ ), and cadmium zinc telluride ( $\text{CdZnTe}$ ) are particularly useful as materials for room temperature radiation detection devices. However, for high radiation detection efficiency it is necessary to have materials that exhibit very low leakage currents (e.g.,  $< 10^{-7}$  A at electric fields of about 1000 V/cm to about 3000 V/cm) and thus, high electrical resistivity (i.e.,  $1/\sigma \geq 10^9$  ohm  $\cdot$  cm). One of the primary problems associated with nonmetallic, crystalline semiconducting materials lies in the presence of charge trapping defect sites and electrical instabilities caused by impurities in the starting material or introduced during subsequent processing. In addition, electrically active impurities may move under the influence of the applied field leading to unpredictable and variable electrical properties including high dark current and spectral distortions. The electrical resistivity of a material is a measure of its purity and defect concentration in the material and for most semiconducting material resistivities much greater than  $10^8$  ohm  $\cdot$  cm require semiconducting materials of the very highest purity and are thus, very difficult to achieve (M. Hage-Ali and P. Siffert, Semiconductors for Room Temperature Nuclear Detector Applications, 43, 245, 1995).

An alternative approach to radiation detection, particularly for the detection of neutrons, is the use of a scintillator material that emits visible light when exposed to radiation. The strong interaction of neutrons with hydrogen containing materials makes them particularly desirable as detector materials for neutron measurements. One method of imaging neutrons employs track detectors such as plastic scintillating fiber bundles externally coupled to photomultiplier tubes or photodiodes to record light and to determine the momentum of recoil protons generated within the scintillator. This approach has inherently high sensitivity due to the strong interaction with the protons of the plastic scintillator material and has been demonstrated for neutron energies down to about 14 MeV. However, charges generated by ionization of the plastic scintillator material must diffuse to specific sites that promote radiative recombination. Losses due to non-radiative recombination, isotropic emission of the scintillation light, attenuation and reflection at interfaces, and spectral mismatch with the photodetector can result in a signal that

can be difficult to detect. Further, tracking recoil protons from typical fission neutrons (neutrons having energies between about 1 MeV to about 10 MeV) requires spatial resolution on the order of about 10 $\mu$ m to about 100 $\mu$ m, which is very difficult to achieve by this approach due to reduction of active volume and light  
5 output for reduced fiber diameter in the bundles (typical diameters are  $\approx$  50 $\mu$ m to 500 $\mu$ m).

Organic materials and particularly organic polymer materials and polyaromatic hydrocarbons are known in the art to possess very high resistance to the flow of direct current and thus should be desirable as a medium for the detection of ionizing  
10 radiation. Moreover, as discussed above, the interaction of ionizing radiation, neutrons, with the hydrogen of organic materials makes these materials particularly suitable as detector materials for detection of ionizing radiation, providing the organic materials possess a high enough electrical resistivity.

#### SUMMARY OF THE INVENTION

15 The present invention is directed to material for detecting ionizing radiation, and particularly for detecting neutrons, and apparatus pertaining thereto for detecting and measuring ionizing radiation. The detection material comprises a class of organic materials,  $\pi$ -conjugated molecules, whose members are intrinsic semiconducting materials and can include  $\pi$ -conjugated polymers, polyaromatic  
20 hydrocarbon molecules capable of charge transfer reactions such as naphthalene, anthracene, and rubrene, and quinolates.

The  $\pi$ -conjugated semiconducting polymer material that comprise the invention possess advantages over conventional radiation detection materials, namely:

- Direct electronic detection of fission neutrons is made possible for the first time due  
25 to the strong interaction of fast neutrons with the hydrogen of the polymer.

- The chemical composition of the polymer material enables electronic dosimeters that represent tissue thereby providing for accurate determination of true biological hazard.

5 - By tailoring the chemical composition, the polymer material can be designed to provide a high degree of radiation specificity.

- Inexpensive radiation detectors can be readily fabricated by methods well known in the art.

10 - Unique structures, such as castings with embedded electrodes can be easily produced thereby enabling new detector designs and methods for tracking, imaging, and spectroscopy of ionizing radiation.

Accordingly, it is an object of this invention to overcome the difficulties associated with the use of metallic semiconducting materials and plastic providing a class of high resistivity organic semiconductor materials useful for detection and tracking of radioactive particles,  $\pi$ -conjugated molecules.

15 Another object is to provide apparatus utilizing the inventive material for the direct electronic detection of fission neutrons.

Yet another object is to provide for electronic tissue equivalent dosimeters.

A further object is to provide radiation detectors having a high degree of sensitivity for specific types of radiation.

20 These and objects of the present invention will become apparent from the description below and accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and form part of the specification, illustrate the present invention and, together with the description, explain the invention. In the drawings like elements are referred to by like numbers.

5 Figure 1 shows an embodiment of the invention.

Figure 2 shows a multi-wire detector array.

Figure 3 illustrates the use of a multilayer polymer detector to track radiation.

Figure 4 shows the response of the invention to alpha radiation from  $\text{Am}^{241}$ .

## DETAILED DESCRIPTION OF THE INVENTION

10 The invention is directed to a unique class of organic semiconducting polymer materials,  $\pi$ -conjugated molecules, and materials made therefrom, useful for the direct detection of ionizing radiation. These materials are characterized by a very high electrical resistivity typically ( $1/\sigma \geq 10^9 \text{ ohm} \cdot \text{cm}$ ), and thus avoid leakage current problems associated with conventional semiconductor or crystalline solid  
15 radiation detection materials. These,  $\pi$ -conjugated materials can include  $\pi$ -conjugated polymers and polyaromatic hydrocarbon molecules capable of charge transfer reactions such as naphthalene, anthracene, and rubrene, and quinolates. Interaction of ionizing radiation with these organic materials produces electron-hole pairs, thereby providing for direct electronic detection by means of electrodes and  
20 associated means for providing an electric field across the  $\pi$ -conjugated material, such as a power supply, thus eliminating the difficulties associated with the use of scintillator materials discussed above.

As a class of compounds,  $\pi$ -conjugated polymers typically contain long chains of alternating single and double carbon-carbon bonds and are characterized by  
25 overlapping of  $\pi$  orbitals across the formal single bonds. Polyacetylenes, are

representative of the class of  $\pi$ -conjugated polymers. Block copolymers, comprising segments of alternating single and double carbon-carbon bonds, and segments containing single carbon-carbon bonds, are also part of the general class comprising  $\pi$ -conjugated polymers. Because of their high electrical resistivities (i.e.,  $1/\sigma \geq 10^9$  ohm  $\cdot$  cm),  $\pi$ -conjugated polymers, and particularly  $\pi$ -conjugated polymers such as polyacetylenes, polyfluorines, polyphenylenes, polypyrrole, polyaniline, polythiophene, and derivatives of the foregoing, such as for example poly(*p*-phenylenevinylene), poly(2,5-dioctyloxy-*p*-phenylenevinylene), poly(1-methoxy-4-(2-ethylhexyloxy)-2,5-phenylenevinylene), poly(3,4-ethylene dioxythiophene), and poly(3-octylthiophene), can function as radiation detection materials that exhibit very low leakage currents.

The principle and operation of the invention is illustrated and exemplified generally by reference to radiation detection device shown in **FIG. 1**. The device **100** can be made by forming a layer of a  $\pi$ -conjugated semiconductor material, such as a  $\pi$ -conjugated polymer or polyaromatic hydrocarbon capable of charge transfer reactions, **110** and attaching electrodes **120**, that can be metals; conducting oxides, such as indium tin oxide; or electrically conducting polymers, to opposing surfaces. Power supply means **130** for providing an electric field across the semiconducting polymer completes the circuit. Layer **110** can also comprise a mixture of a  $\pi$ -conjugated polymer and another organic polymer to provide desired physical or chemical properties such as greater mechanical strength and formability. An obvious modification of this device is the use of a three electrode geometry as well as depositing polymer material **110** onto the surface of one electrode and subsequently attaching the second electrode to the free surface of the polymer.

Radiation striking semiconducting polymer material **110** forms an electron/hole pair that migrates, under the influence of the electric field, to electrodes **120** and is detected in an external circuit (not shown). The inventors have contemplated depositing a layer of the semiconductor polymer material onto a silicon wafer having

prefabricated pulse detection circuitry. The electrode/semiconducting polymer combination can be patterned using any technique familiar to those skilled in the art, such as lithography, shadow masking, or selective deposition.

The semiconducting polymer layer can be made by methods known to those skilled in the art including spin or drop casting, melt casting, chemical vapor deposition, injection molding, air brush, ink jet printing, extruding, and in-situ polymerization. Further, by using art known methods, a layer of semiconducting polymer material having thicknesses in the range of between about 10 $\mu$ m to about 100 $\mu$ m can be easily fabricated. These thin polymer layers and their associated electrodes can be stacked one atop the other thereby providing for multi-layer detector arrangements

Because the semiconducting polymers can be cast, it is now possible to make unique radiation detector structures such as illustrated in **FIG. 2**, which shows an array of wire electrodes **310** and **315** embedded in  $\pi$ -conjugated polymer material **110**. The wire array comprises a first set of parallel wires **310** intersecting orthogonally with a second set of parallel wires **315**. Each set of wires is supplied with a device (not shown) for detecting the signal generated when an electron strikes a wire.

Hydrogen has enhanced sensitivity for neutrons having energies between about 1 MeV to about 10 MeV. However, to successfully track fission neutrons having this range of energies a spatial resolution of about 10 $\mu$ m to about 100 $\mu$ m is required. Consequently, by spacing the wire electrodes at a distance of about 10 $\mu$ m – 100 $\mu$ m apart, the device of **FIG. 2** provides a means to track recoil fission neutrons. The ability to detect 1 MeV to 10 MeV fission neutrons is an improvement over prior art radiation detectors which are limited to neutron energies greater than about 14 MeV.

An obvious modification of the device shown in **FIG. 2** is a multi-layer geometry, i.e., a plurality of single  $\pi$ -conjugated polymer/wire arrays is stacked to make a three-dimensional structure. As a neutron penetrates through each layer of the



multi-layer detector a signal is generated. By knowing the layer number and the location of the signal in the layer, and the signal strength it is now possible to determine the direction the fission neutron is travelling.

An example of the use of a multi-layer polymer detector for tracking lower energy particles (i.e., particles having energies between about 1 MeV to 10 MeV) is illustrated in **FIG. 3**. Electrodes **120** or wire electrodes **310** and **315**, spaced between about 10 $\mu$ m to about 100 $\mu$ m apart form, in effect, a plurality of  $\pi$ -conjugated polymer layers that are  $\approx$  10 $\mu$ m to 100 $\mu$ m apart and thus, provide the spatial resolution required to track fission electrons having energies over the range of about 1 MeV to 10 MeV.

A second example of the use of a  $\pi$ -conjugated polymer/electrode array, such as that illustrated in **FIGs. 1** and **2**, provides for detecting (d,t) reactions, an option heretofore unavailable.

In addition to making possible the production of very small devices and three-dimensional devices, the  $\pi$ -conjugated polymer material can be cast into sheets capable of covering large areas, in contrast to prior art semiconductor and crystalline solid radiation detector materials which are limited to an area of a few cm<sup>2</sup>. These sheets of polymer radiation detector material can be deposited onto flexible electrodes and rolled up to form a radiation detector occupying a small volume but having a large surface area, an application impossible with conventional radiation detector materials.

The ability to produce thin sheets of the  $\pi$ -conjugated polymer materials as well as the ability to produce these materials with the same C:H ratio and density as human skin now makes it possible to produce an electronic tissue equivalent dosimeter. Moreover, by making the tissue equivalent dosimeter as massive as possible it can be made more sensitive. This dosimeter can measure not only the total absorbed dose but also how much tissue damage would be done by the

ionizing radiation from the track length of the radiation in the polymer material (dE/dx).

Physical properties of organic polymer molecules, such as electrical resistivity, can be changed by changes in the structure of the polymer. By way of example, when a polymer is crystallized in the absence of an applied external force there is no preferred orientation of the polymer chains. If such an unoriented polymer is subjected to an external stress, typically above the polymer glass transition temperature but below the melting temperature, it undergoes a rearrangement in the direction of the applied stress causing a marked change in physical properties. In addition, the polymer changes from an isotropic to an anisotropic material. In general, a property such as the electrical resistivity decreases in the orientation direction and increases in the direction transverse thereto. Thus, the resistivity of the semiconductor polymer material can be tailored by stretching or generally deforming the polymer.

In addition to changing the resistivity of the semiconducting polymer material by application of stress, it is also possible to enhance the ability of these materials to detect specific radiation by incorporating metals such as aluminum, gallium, lithium, in the form of lithium salts of carboxylates, and boron, in the form of boronic acids, into the polymer structure.

The invention will be illustrated and exemplified by means of the example below.

#### EXAMPLE

An electrode was prepared by sputtering a 1 $\mu$ m thick metal film onto a glass substrate. An amount of poly(3-octylthiophene) was dissolved in either toluene or chloroform to form a 10 vol% solution. An inert polymer, such as polystyrene or poly(methyl methacrylate), can be added to the solution (about 10% of the amount of poly(3-octylthiophene)) to improve the mechanical properties of the dried polymer. The solution as spin cast at about 500 RPM onto the electrode surface to form a film

about 25 $\mu$ m to about 100 $\mu$ m thick and the electrode/polymer composite was baked below 100°C to remove the solvent. A second electrode was sputtered onto the surface of the organic polymer film to form a radiation detector device. A power supply was attached to the radiation detector structure and a measurement of the device response to alpha radiation was made.

A detector device prepared as in the example above was exposed to alpha radiation from an  $\text{Am}^{241}$  source and response of the detector was measured. The results are shown in **FIG. 4**. Very strong signal pulses were recorded at a modest bias voltage (50 V, corresponding to a field of about  $10^6$  V/m). The detector performed well up to bias voltages of 140 V. Above about 200 V, spurious pulses were observed, possibly caused by dielectric breakdown or field emission near the edge of the device. The polymer withstood voltages of over 1000 V with no evidence of permanent damage.

In summary, the present invention is directed to a class of materials, namely  $\pi$ -conjugated materials including polymers, polyaromatic hydrocarbons, and quinolates, which because of their semiconducting properties and high electrical resistivity can be used for radiation detection, and to fabricate radiation detection devices.